PB82-162876

A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards Standard Reference Materials

(U.S.) National Bureau of Standards
Washington, DC

Prepared for

Environmental Monitoring Systems Lab.
Research Triangle Park, NC

Jan 81

U.S. Department of Commerce
National Technical Information Service
NTIS

NBS

EPA

National Bureau of Standards
Gas and Particulate Science Division
Washington DC 20234

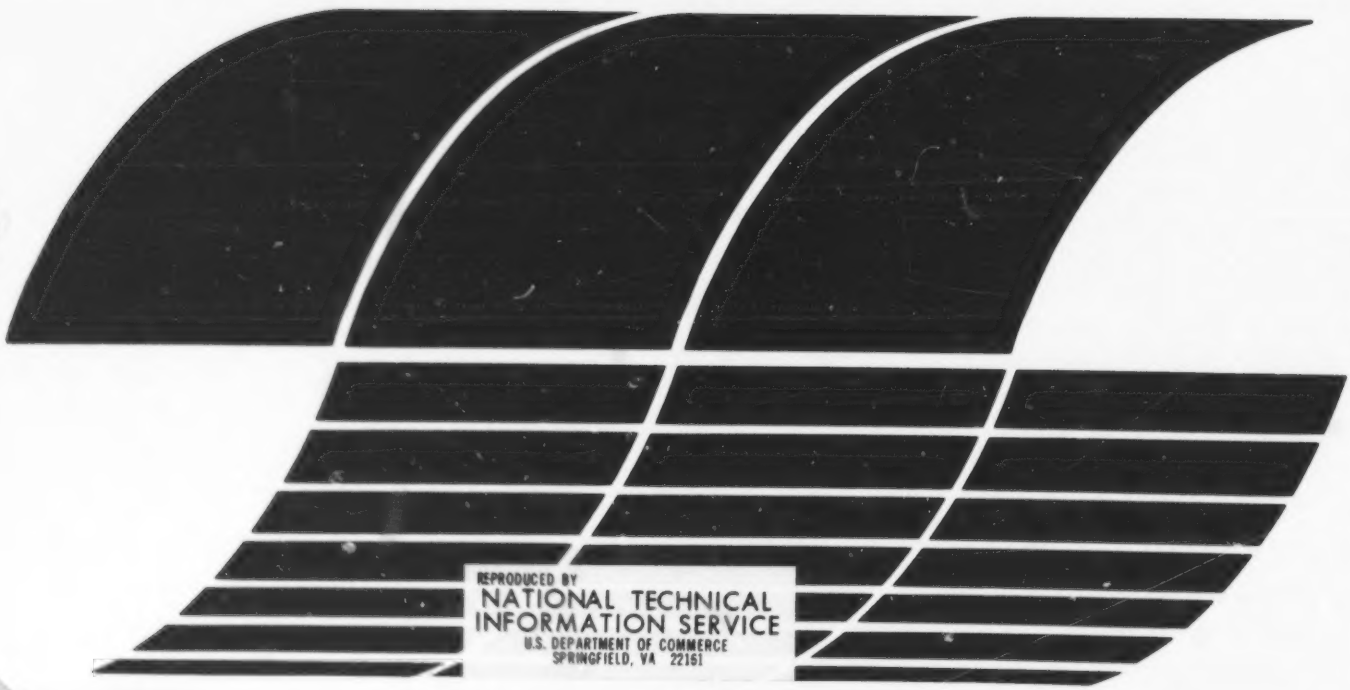
PB82-162876

United States Environmental Protection Agency
Office of Environmental Processes and Effects Research
Washington DC 20460

EPA-600/7-81-010
May 1981

Research and Development

A Procedure for Establishing Traceability of Gas Mixtures to Certified National Bureau of Standards SRMs



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1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/7-81-010		PB82 162876

4. TITLE AND SUBTITLE	5. REPORT DATE
A PROCEDURE FOR ESTABLISHING TRACEABILITY OF GAS MIXTURES TO CERTAIN NATIONAL BUREAU OF STANDARDS STANDARD REFERENCE MATERIALS	January 1981
	6. PERFORMING ORGANIZATION CODE 041059
7. AUTHOR(S) Ernest Hughes and John Mandel	8. PERFORMING ORGANIZATION REPORT NO. NBSIR 81-2227
9. PERFORMING ORGANIZATION NAME AND ADDRESS National Bureau of Standards, Washington, DC 20234 U.S. Environmental Protection Agency Office of Research and Development, EMSL Research Triangle Park, NC 27711	10. PROGRAM ELEMENT NO. GAP-1AAF60E10N 11. CONTRACT/GRANT NO. EPA-IAG-D8-E684
12. SPONSORING AGENCY NAME AND ADDRESS Jointly Sponsored by: National Bureau of Standards, Gaithersburg, MD U.S. Environmental Protection Agency, EMSL, RTPNC	13. TYPE OF REPORT AND PERIOD COVERED Final 14. SPONSORING AGENCY CODE EPA/ORD/17

15. SUPPLEMENTARY NOTES
This project is part of the EPA-planned and coordinated Federal Interagency Energy/Environment Research and Development Program.

16. ABSTRACT

This procedure includes the specifications and requirements that must be followed by gas manufacturers during the preparation of compressed cylinder gas Certified Reference Materials (CRM). A CRM is a certified gas standard prepared at a concentration that does not exceed ± 1 percent of currently available National Bureau of Standards Standard Reference Material (SRM) cylinder gases. The procedure includes specifications and requirements for: (1) preparation of compressed gas samples in cylinders prepared in lots of ten or more of identical concentration with the average concentration for the lot within ± 1.0 percent relative to the concentration of a specific SRM; (2) tests to verify compressed gas samples stability and within lot homogeniety; (3) simultaneous submission by the gas manufacturer of analysis results to NBS and cylinder gas numbers to USEPA (without analysis results); (4) random selection by USEPA of two cylinders per lot for an USEPA performance audit analysis; (5) submission by USEPA of audit results to NBS, and (6) decision by NBS whether to allow the gas manufacturer to sell the lot of cylinders as CRM. A procedure for CRM for CO in N_2 or air is described as Appendix C. Future appendices will be added for other CRM including NO in N_2, SO_2 in N_2, CO_2 in N_2, and O_2 in N_2.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Traceability, Certified Gas Standards, Nitric Oxide, Sulfur Dioxide, Carbon Dioxide, and Oxygen		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	43
	20. SECURITY CLASS (This page)	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

Errata

Cover Title: "A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards SRM's"

Page 4 — All (+) in the 3 equations should read (-).

Page 7 — Line 8. "Cyliners" should read "Cylinders"

Page 20 — Par. B, diagram, "Internal Response Standard" should read "Internal Reference Standard"

Page 21 — Equation 6 should read: $\hat{C}i = Ri \, \bar{S} \, \frac{Co}{So}$

Page 24 — Equation should read:

$$\left| c_1 - c_1^* \right| \leq 2 \sqrt{q_{c_1}^2 + q_{c_1^*}^2}$$

EPA-600/7-81-010
January

A PROCEDURE FOR ESTABLISHING TRACEABILITY OF GAS MIXTURES TO CERTAIN NATIONAL BUREAU OF STANDARDS STANDARD REFERENCE MATERIALS

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NBSIR 81-2227

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ABSTRACT

A procedure is described by which the concentration of commercially produced gas mixtures may be related to certain Standard Reference Materials (SRM's) currently offered by the National Bureau of Standards. The concentration of the gas mixture, the Certified Reference Material (CRM) must be close to the concentration of a particular SRM in order to reduce the error involved in the comparative analysis. Statistical treatment of the traceability process is given by an example as is the process by which a body requiring traceability can evaluate the quality of the CRM.

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FOREWORD

The role of the National Bureau of Standards in the Interagency Energy/Environment R&D Program, coordinated by the Office of Research and Development of the U. S. Environmental Protection Agency, is to provide those services necessary to assure data quality in measurements being made by the Federal, state, local, and industrial laboratories participating in the interagency program. The work at NBS is coordinated by the Office of Environmental Measurements and is conducted in the Center for Analytical Chemistry, the Center for Radiation Research, and the Center for Thermodynamics and Molecular Science. NBS activities form part of the Characterization, Measurement, and Monitoring Program Category and address the data quality assurance needs of air and water monitoring programs. NBS efforts in support of data quality assurance include:

- Studies of the feasibility of production of Standard Reference Materials which could be used for the verification of performance audit samples for quality control programs or used for the calibration of field and laboratory instruments.
- The development and demonstration of new or improved measurement methods, particularly when needed for the certification of Standard Reference Materials.
- The evaluation and dissemination of data on the physical and chemical properties of effluents, products and raw materials of environmental significance in energy production.
- The provision of reference materials for the evaluation and validation of monitoring methods.

This report is one of the Interagency Energy/Environment Research and Development Series Reports prepared to provide detailed information on the development of an NBS measurement standard or method.

WILLIAM H. KIRCHHOFF, Chief
Office of Environmental Measurements
National Bureau of Standards

1. INTRODUCTION

This procedure is intended to increase the availability of accurate gas standards by the creation of a series of secondary standards, to be referred to herein as "Certified Reference Materials" (CRM's). The CRM's prepared according to this procedure will be related, within known limits of uncertainty, to specific gaseous Standard Reference Materials (SRM's) offered by the National Bureau of Standards. The CRM's are intended to supplement the supply of existing SRM's and are not intended to offer traceability for gas mixtures at concentrations other than those of the complementary SRM's nor of gas mixtures containing components other than those in the SRM's.

The procedures described are based on experience at NBS relative to the production and certification of gaseous SRM's and are intended to assure reliable CRM's with reasonable effort but are not intended to reduce the effort to a minimum. The acceptance of the CRM's by regulatory agencies, by industry, and by other users, will depend on the reliability of the CRM which in turn will depend on the integrity of the gas supplier relative to the methods, conditions, and limitations of the procedure described here and on the reliability and extent of any complementary audit program.

2. CERTIFIED REFERENCE MATERIALS

2.1 Description

The CRMs will consist of compressed gas samples in cylinders prepared in lots of ten or more of identical concentration. The average concentration for any lot must lie within ± 1.0 percent relative of the concentration of a specific SRM, but preferably the concentration should be as close as technically possible to the SRM in order to reduce to a minimum any errors which might arise in subsequent analyses of the CRMs. The concentration for a specific CRM will be determined by analysis with a specific SRM and the uncertainty assigned to the concentration of the CRM will consist of the uncertainty of the SRM and the added uncertainty resulting from the intercomparison of the CRM to the SRM. The period of time during which the concentration of the CRM is certified, and the presence of any impurities of consequence will be reported by the supplier.

2.2 Preparation

The CRM's will be prepared in lots of at least ten (10) cylinders all filled from an homogeneous bulk mixture prepared in a single container or in several containers ganged together in such a manner that delivery occurs simultaneously from the several containers or by use of a dynamic blending system. The reagent gases with which the bulk mixture is prepared must be analyzed for the major component(s) and for minor constituents of interest. The concentration of the component of interest in the bulk mixture must lie within ± 1 percent relative of the particular SRM which is being duplicated. The cylinders into which the bulk mixture is transferred and which will become the CRM's must be clean, of known compatibility and history, and must be treated to assure stability of the mixtures which will be contained. The cylinders will be equipped with valves of appropriate material which conform to Compressed Gas Association (CGA) recommendations for the particular gas mixture.

After filling, an "incubation" period must be allowed before final analysis. This period will vary depending on the nature of the gas mixture and will be described in the appendices.

2.3 Analysis

The analysis consists of a comparison of each CRM to the appropriate SRM. The requirement that the CRM have a concentration within ± 1 percent relative of the SRM reduces the error arising from the intercomparison and simplifies the calibration procedure for the analytical instruments. In most cases the characteristics of the analyzer are such that the response of

the instrument over a small concentration range (1 percent relative or less) can be described by the linear equation

$$y = mx + b$$

where y is the signal, m is the instrument sensitivity in signal units per unit of concentration, x is the concentration and b is a constant in signal units. Consequently, it is only necessary to determine that the sensitivity does not change significantly over the interval between the concentration of the CRM and the SRM in order to compare the two signals directly. It follows then that the closer in concentration are the CRM and SRM, the less possibility exists of error in assigning a value to the CRM.

The general characteristics of the analyzer response relative to concentration is determined by constructing a calibration curve using the SRM against which the CRM is to be compared as one calibration point and at least two other gas mixtures for a minimum of three calibration points. These additional calibration gases should be SRM's, one higher in concentration and one lower in concentration as compared to the SRM which is being used to analyze the CRM. Obviously this is not possible when the CRM is being compared to either the highest or lowest concentration SRM in a particular series. In this case, the CRM should preferably have a concentration slightly lower than the SRM, if it is the highest SRM in a series, or slightly higher if the SRM is the lowest in a series. If the SRM is the lowest in a series, the use of a "zero" gas may be feasible. However, either the use of a zero gas or extrapolation beyond the calibration curve established with SRM's should be done with caution.

The ideal case where the instrument response over a wide range is directly proportional to concentration can be readily recognized by measuring the signal generated by the three SRM calibrating gases and dividing each by concentration to obtain the sensitivity (m) at the three concentrations. If the response is linear and if the calibration line passes through the origin, the value for M will be the same at all three concentrations and the equation reduces to y = mx. If m is constant over a wide range of concentrations, then it follows that it will be constant over a smaller range. In this case, the concentration of the CRM is simply

$$C_{CRM} = \frac{I_{CRM}}{I_{SRM}} C_{SRM} \qquad \text{or}$$

$$C_{CRM} = \frac{I_{CRM}}{m} \qquad \text{since}$$

$$m = \frac{I_{SRM}}{C_{SRM}}$$

where I is the signal generated by either the SRM or the CRM and C is concentration.

In the somewhat less ideal case where the response is linear but does not pass through the origin, the value of the signal divided by the concentration will not be equal at the three concentrations but a straight line of slope m and intercept b can be fitted to the data. It again follows that if m is constant over a wide range of concentrations, it will be constant over a small interval and the concentration of the CRM is expressed as

$$C_{CRM} = \frac{I_{CRM} + b}{I_{SRM} + b} C_{SRM} \qquad \text{or}$$

$$C_{CRM} = \frac{I_{CRM} + b}{m} \qquad \text{since}$$

$$m = \frac{I_{SRM} + b}{C_{SRM}}$$

A third case is that of an analytical instrument with non-linear response. In this situation a calibration curve is constructed using at least three SRM's and the concentrations are determined using the derived equation for the curve. In most cases the component in a CRM which is being analyzed will be measured with an instrument which is essentially linear over small ranges of concentration. In other words, the sensitivity of the instrument — the response in signal units per unit of concentration — will not change within the limits of precision of the instrument over short intervals of concentration. If the sensitivity is found to be essentially constant over the internal of ±1% of the concentration of the SRM which is to be reproduced by the CRM then the sensitivity measured for the SRM can be used to calculate the concentration of the CRM. In this case, the closer the CRM is in concentration to the SRM the smaller will be the error introduced by assuming short range linearity.

It is essential in analyzing the CRM's that the analyses be made with the highest degree of precision possible in order that the total uncertainty of the concentration of the CRM be not appreciably larger than the total uncertainty of the concentration of the SRM with which it is compared.

The principal elements which contribute to the imprecision of this comparison include sensitivity and instrument instability. The sensitivity of the instrument should be high enough so that differences of concentration of 0.1 percent relative can be measured. Instruments are available which are capable of measuring all current SRM's with this sensitivity. However, most instruments exhibit drift to one degree or another. The drift has two components, short term drift or noise and a longer term drift characterized by a slowly changing signal under constant operating conditions. The effect of short term drift can be minimized by a number of techniques including the multiple analyses of each sample, and signal averaging. The effect of long term drift can be minimized by frequent calibration of the instrument. The characteristics of each analytical system should be considered individually to determine the optimum frequency of calibration and the

approach to compensation or control of the effect of noise. However, it should be noted that the effort expended in minimizing these effects will be reflected in the precision of the analyses relating the CRM to the SRM. In general, if duplicate analysis of single samples consistently agree within ± 0.1 percent relative, then the effect of noise is at an acceptable level and if repeated analysis of the same sample performed at intervals during the analysis of a lot agree within the same limits, then the long term drift is at an acceptable level.

3. SUGGESTED ANALYTICAL PROCEDURE

3.1 Description

The analytical procedure recommended here is considered to be the minimum effort necessary to adequately reduce the possibility of accepting an unstable CRM. All CRMs must be stable and each batch should be homogenous. An unstable batch must be rejected while an inhomogenous batch may be acceptable providing that the reason for the inhomogeneity is known and further providing that the cause of the inhomogeneity will not result in a future change in concentration not revealed by the test for stability.

The object of the analysis is to compare a lot of at least ten samples of presumably identical concentration to an SRM and to express the concentration of each sample in the lot with error limits defined by the uncertainty of the SRM and the uncertainty added by the analytical procedure. Obviously the simplest procedure would involve direct analysis of the CRM with the SRM but with most analytical methods this approach would be unduly extravagant in terms of SRM consumption. Consequently, it is recommended that the concentration be determined on a relative basis by comparing one sample from the lot to all others in the lot. Thus only the one sample is compared to the SRM and the concentration of all others in the lot can then be determined from the measured ratio of each to the one sample. An additional uncertainty is introduced in this procedure but the size of this uncertainty can be reasonably small and the final uncertainty in the CRM will not be increased significantly.

The sample from the lot with which the rest of the lot is to be compared, the internal standard, is selected at random from the lot. The signal generated by the internal standard is compared to the signal generated by each sample. The internal standard is repeated throughout the sequence of analysis so that any long term instrument drift can be compensated for if necessary.

The resulting data can be expressed as the ratio of the signal generated by the individual CRM's to that generated by the internal standard. The ratio in all cases should be very close to 1.000 if the lot is homogenous.

3.2 First Analysis

An initial analysis of the batch of CRM's should be performed as soon as practical after the preparation of the CRM's. A sample is selected at random from the lot to serve as the internal standard to which a number of samples from the lot are compared. At least ten samples selected at random from each lot should be analyzed during this first analysis. However, if the lot is small (< 20 samples) it is recommended that all samples be analyzed.

The internal standard should be analyzed during the first analysis to confirm that the concentration lies within ± 1 percent relative of the appropriate SRM and to establish a reference for later analyses intended to define the stability of the lot. The internal standard should be analyzed at least ten times using SRM's to calibrate the instrument. Each of the remaining nine or more samples selected is then analyzed in duplicate, using the internal standard as a reference.

Some preliminary conclusions regarding the homogeneity and stability of the batch may be drawn from the results of the first analyses. For instance, if the batch was homogenous when transferred and if no subsequent reactions have occurred randomly in the cylinders, the concentration of all samples analyzed should be the same within the limits of precision of the analytical method. The appropriate statistical treatment at this step is given in the appendices. If the statistical test shows lack of homogeneity between the samples, it is not possible at this time to determine whether such inhomogeneity is due to improper preparation or to reaction in the cylinders. If the test shows reasonable closeness among the results for all samples, then there is some assurance that the batch is homogenous.

If the analyses at this point indicate that no serious problem exists, the entire batch is set aside for the required "incubation" period. If, however, the batch appears to be somewhat inhomogeneous the analyses should be continued to include all samples in the batch. An analysis of each sample at this time may become critical later in differentiating inhomogeneity resulting from preparation and inhomogeneity arising from instability.

3.3 Second Analysis

After the required incubation period has passed, all of the samples in the lot are analyzed including those analyzed during the first analysis. The first analysis served to define the concentration of the CRM and to test the stability and homogeneity on a qualitative basis. Final decisions regarding these factors depend on the second and more extensive analysis. Sufficient time will have elapsed so that reactions in individual cylinders which were of too low a rate to be recognized by the distribution of concentrations in the initial sample lot, will be revealed by this subsequent analysis. Decisions regarding homogeneity which may have been based on analysis of a portion of the batch will now be based on results obtained on the entire batch.

3.3.1 Stability and Homogeneity

The stability of the lot is assumed if the concentration of each CRM included in the first analysis has not changed appreciably at the time of the second analysis (see Appendix A). An inspection of the data of the first and second analyses may reveal gross instability and if such is found the lot should be discarded.

In a lot consisting of cylinders prepared by transfer of a single bulk mixture to a number of smaller containers, the composition of the gas in all the smaller cyliners should be identical. Differences observed between cylinders should reflect only the random errors in the analytical process. Differences greater than this random error arise from two sources. First, there are the differences which result from faulty mixing or from dilution by residual gases left in the cylinder prior to transfer of the bulk mixture. The second and more critical source arises from reactions, chemical or physical, which occur in the cylinder after transfer. Because these reactions are largely due to wall effects and because no two cylinder walls are alike, the reactions generally proceed at different rates in different cylinders. The two effects may be differentiated one from the other by sets of measurements made over a period of time sufficiently long so that the extent of reaction is greater than the error in the analysis. For instance, if a lot is analyzed immediately after preparation and individual samples are found to have concentrations that vary more than can be accounted for statistically by analytical error, then the mixture is either inhomogenous or some or all samples in the lot are unstable. If the lot is reanalyzed after some time and each sample has retained essentially its previous value then the samples are probably stable but the lot is inhomogenous. If the concentration of one or more of the samples has changed significantly, then it is plausible to conclude that the lot is unstable.

An inhomogenous lot need not necessarily be discarded but an unstable lot must be discarded. An inhomogenous but stable lot in which the range of values does not exceed ± 1 percent of the value of the SRM with which it is to be compared may be used providing the reason for the inhomogeneity is determined and that the cause does not otherwise affect the integrity of the CRM. A lot prepared by transfer from a single bulk container should be homogenous. If the bulk container consists of several large cylinders ganged together to allow simultaneous delivery, then some inhomogeneity may arise if the concentrations in the several bulk containers differ slightly. In the special case of large scale dynamic dilution systems where two components are mixed under constant flow conditions and are then compressed into the cylinders in the lot, some inhomogeneity may result depending on the design of the delivery system. If variations in concentration are observed in a lot prepared by this method, the variation may be related to the position of individual cylinders on the manifold and it is therefore important to record the position of each cylinder for possible future reference.

It should be reemphasized at this point that all samples in a batch which is not entirely homogenous should be analyzed both during the first and second analysis. It is essential that in cases where the samples are stable but not entirely identical in terms of concentration, each sample be certified separately as an individual.

The nature of the distribution of the concentration of samples in a lot may give significant information concerning both the homogeneity and stability of the lot. A lot which has concentrations that vary no more than can be accounted for by the errors of the analytical method, is probably homogenous and stable. A lot in which the range of values exceeds significantly what might be expected on the basis of analytical error and in which several samples are considerably below the average, probably is unstable. A lot in which the range of values is large but all concentrations are essentially symmetrically distributed around the average, was probably not prepared or transferred in such a way that homogeneity was assured. A lot may be found with concentrations grouped around two or more average values (bimodal or multimodal distributions). This usually results from errors in the gas blending or transfer operations. It should be noted, however, that the detection of such situations is, except for very large numbers of cylinders, statistically very uncertain. Occasionally a single sample in a lot will be found with a concentration appreciably below the average for the lot. A single such sample probably represents a fault in the preparation or filling of the cylinder and may be omitted from the lot providing the lot is otherwise stable and homogenous. The presence of more than one outlier in a lot or the occurrence of a single outlier in several lots should be cause for concern and in the absence of a reasonable explanation for the multiple outliers, the lots should be remade.

All of the evidence at this point must support the assumption that the lot is stable, reasonably homogenous and that it meets all other requirements for a CRM. If there is any suspicion that the lot may be unstable or inhomogenous, then further analytical work should be conducted before a final decision is made.

3.3.2 Estimation of the Uncertainty of the CRM

The estimated uncertainty of the CRM is composed of at least three components: the uncertainty of the SRM with which the CRM is analyzed, the imprecision of analysis of the internal standard with the SRM, and the imprecision of analysis of the CRM's with the internal standard. A discussion of the statistical procedure for estimating and combining these three sources of error will be found in the appendices. Here we merely mention that the second component is evaluated on the basis of the ten or more measurements of the concentration of the internal standard, and that the third component is evaluated from the variability of the results of all samples in the lot. From the combined variability of these three sources, an upper limit for the uncertainty of the concentration can be calculated for each individual sample, for use in the certificate accompanying the sample.

4. AUDIT OF THE CRM

4.1 Introduction

At this point the producer should have sufficient evidence to make a decision as to whether or not the batch will qualify as a CRM. This decision must be based on the measured stability and homogeneity and on the fact that the measured concentration of any sample in the batch lies within ± 1 percent relative of the complementary SRM. The evidence for compliance with the requirements for a CRM may be so overwhelming that a visual examination of the data may convince the producer that all is well. However, the final decision must await the results of an independent examination of the data and of an independent analysis of at least some of the samples. This independent analysis will be referred to as the "audit program". Upon its completion, the data of the producer and those resulting from the audit will be intercompared, using appropriate statistical procedures of data analysis which are described in the appendices.

4.2 Environmental Protection Agency Audit Program

The purpose of the Audit Program is to determine whether or not the CRM's in a particular lot are of the concentration claimed by the producer. This will be determined by an analysis of two or more samples from the lot. The analysis will be performed by a laboratory chosen by the Environmental Protection Agency (EPA). Analytical results obtained by the auditor and the producer will be submitted to the National Bureau of Standards for evaluation. If the results of the analysis by the auditor confirm the analysis claimed by the producer, the EPA will be so informed. If the results do not agree, either the auditor or the producer (or perhaps both), will be asked to repeat the analysis. If this additional analysis demonstrates the validity of the producer's value, the EPA will be so informed. If, however, there is still disagreement, the samples will be submitted to NBS for analysis. The auditor may be required to analyze the CRM's for substances other than that for which it is certified depending on the requirements specified in the appendix concerning the particular substance.

4.2.1 Selection of Samples

The producer will submit a list of samples identified by sample number and cylinder number to the auditor. The auditor will select two samples at random which the producer will then send to the auditor. The producer will inform the auditor of the particular SRM which the CRM is intended to duplicate. This SRM will be identified by SRM number, sample number, cylinder number and date of purchase.

4.2.2 Analysis

The analysis of the CRM will be performed with an instrument whose response characteristics are known at the concentration of the CRM. The auditor will calibrate the instrument using SRM's, one of which must be of the same nominal concentration as the CRM. The number of other SRM's used in the calibration will depend on the characteristics of the instrument but should include at least two others. The auditor must be able to demonstrate the validity of the calibration of the instrument in the concentration range between the SRM and the CRM.

Each sample will be analyzed ten times with the calibrated instrument. The procedure and sequence of analyses will be planned by the auditor and should be such that a high degree of precision is obtained.

The average concentration for each sample and the standard deviation are to be reported. In general, the precision of the methods used in the analysis of gas mixtures of a type represented by the CRM should yield standard deviations which do not exceed 0.5 percent relative. If this value is exceeded, then the procedure should be carefully examined for sources of imprecision and the analyses should be repeated. In calculating the average and the standard deviation of the ten measurements for each sample, it is not permissible to omit or change any values (possible "outliers") except where experimental conditions were known to be inappropriate during the measuring process.

4.2.3. Report of Results

Both the producer and the auditor will submit to NBS a comprehensive report of their analyses. Each individual analysis result for each of the samples analyzed shall be reported. The producer will also report the SRM's, identified by number, sample number, cylinder number, concentration and purchase date, which were used in the calibration of the instrument. A brief description of the method, the calibration procedure and the measured instrument sensitivities at the calibration points will also be submitted.

The auditor will submit the individual result of each analysis on each of the two samples, with information concerning the SRM's used, the instrument employed, the calibration procedure and any other analytical results obtained as may be required for the particular mixture.

The report may be made on the forms shown in the appendices or by letter containing the same information.

4.3 Examination of Results

The analytical data submitted by the producer will be examined by NBS to assess the homogeneity and stability of the batch. The results reported by the auditor will be used to confirm or reject the concentration claimed by the producer. It is assumed that an unstable lot would be readily evident to the producer and would not have been retained for use as CRM's. It is further assumed that an inhomogeneous lot would be recognized and would not be retained except in the very special case where the reason for the inhomogeneity was known and where the stability was unequivocally demonstrated. Such batches will be individually considered and further analyses may be requested of the producer.

4.4 Certification

If the particular batch of CRM's is reasonably homogenous and definitely stable and if there is no significant difference between the concentration claimed by the producer and that found by the auditor, both the EPA and the producer will be notified. The producer may then certify the samples in that particular batch as having met the requirements of a Certified Reference Material.

In order to assure the purchaser of a CRM that it has been prepared according to the procedures described herein, and that the results of the EPA audit and the NBS analysis of the analytical data confirm the producers concentration within acceptable limits, the producer will supply the purchaser with the following:

1. A copy of the letter from NBS to EPA and to the producer stating **that the particular lot meets the requirements** for CRM's. The letter will list each cylinder in the lot identified by cylinder and sample number and will show the producers value for the concentration of each sample in the lot. In addition the letter will identify the samples audited by EPA and will give the concentration determined by the audit.

2. A producers "Certificate of Analysis" which will include as a minimum the cylinder and sample number, the concentration for the particular sample and the uncertainty assigned to that concentration. In addition, the period of certification and the date of the beginning of the period will be given. Finally, the certificate will identify the NBS-SRM used by the producers to establish traceability of the CRM.

APPENDIX A

Statistical Analysis of Data

I. Introduction

The data submitted to NBS by the producer and the auditor will be examined in detail to determine that the candidate lot of CRMs is of the concentration claimed and that the lot is stable and homogenous. The statistical treatment is illustrated in this appendix by means of an example based for the most part on real experimental data. However, it was necessary to synthesize some data, particularly in describing the auditor results, to produce an example illustrative of the whole process. It should be noted that this example does not define the degree of measurement precision required of a CRM and in many cases the precision shown would not be attainable because of such factors as instrument sensitivity and the chemical and physical properties of the gases involved.

II. Illustrative Example and Statistical Analysis

1. Producer's Calibration Data:

The producer provided the following data on the calibration of his instrument:

TABLE 1.

SRM No.	Concentration*	Signal or Sensitivity
1677	9.67 ± .09 ppm	11.51 mV (signal)
1678	44.9 ± .5 ppm	54.10 mV (signal)
1679	97.1 ± .9 ppm	114.86 mV (signal)

* The ± values are the total uncertainties given in the SRM certificates.

A linear regression of signal vs. concentration provides the equation:

$$\text{signal} = .464 + 1.181\ (\text{concentration})$$

The fit to the straight line is good, and is only minimally affected by making the intercept zero. This leads to the modified equation:

$$\text{signal} = 1.187\ (\text{concentration})$$

The fit provided by this equation is shown in the following table where the fitted values in the last column should be compared with the observed values of signal:

TABLE 2

Signal	
Observed	Fitted
11.51	11.48
54.10	53.30
114.86	115.26

We conclude that the instrument gives essentially a linear response and is in good state of calibration. However, since the samples to be analyzed have a concentration close to that of SRM 1678 (about 45 ppm), a sensitivity value can be adopted that is based on a calibration line going through the origin and through the point whose abscissa is the certified value of SRM 1678 and whose ordinate is the measured value for this SRM. This gives the calibration equation which will be used for all further analyses:

$$\text{signal} = 1.205\ (\text{concentration})$$

2. Analysis of Internal Reference Standard

One of the cylinders was selected as an Internal Reference Standard. The measurements,* in mV are shown in the second column of Table 3. The third column shows the concentration values, in ppm, obtained by using the sensitivity 1.205 mV/ppm for the conversion.

TABLE 3

Measurement No.	Signal (mV)	Concentration (ppm)	Measurement No.	Signal (mV)	Concentration (ppm)
1	53.7623	44.616	6	53.7683	44.621
2	53.7382	44.596	7	53.7454	44.602
3	53.7454	44.602	8	53.7237	44.584
4	53.7948	44.643	9	53.7707	44.623
5	53.7719	44.627	10	53.7767	44.628

The average concentration for the Internal Reference Standard is:

$$\bar{x} = 44.6139 \text{ ppm}$$

with a standard deviation among single replicate measurements of

$$s_x = .018 \text{ ppm}$$

The standard error of the average value for this cylinder is:

$$s_{\bar{x}} = \frac{.018}{\sqrt{10}} = .0057 \text{ ppm}$$

* Note: It is not required that either producer or auditor provide the actual measured value of the signal. However, the value of the concentration calculated from the signal should be expressed with sufficient digits to reflect the magnitude of the signal. In other words, don't round off the calculated concentration when submitting the data for evaluation.

3. Analysis of All Samples

The Internal Reference Standard is now used by the producer to analyze all the cylinders in the lot. This is generally accomplished by measuring the ratio of the signal for the sample to that for the internal standard. Table 4 shows the signal ratios, denoted R, and the corresponding calculated concentrations, denoted C, using the value 44.6139 ppm for the internal standard. Thus, each concentration is obtained by the equation:

$$C = R\ (44.6139)$$

where

$$R = \frac{\text{signal for sample}}{\text{signal for internal standard}}$$

TABLE 4

Sample	First Analysis R	First Analysis C	Second Analysis R	Second Analysis C	Difference between Duplicates
5	1.000177	44.622	.999601	44.596	.026
6			1.000592	44.592	
11			1.000592	44.640	
13	1.000102	44.618	1.000406	44.632	-.014
15			1.000392	44.631	
21			.999482	44.591	
23	1.000904	44.654	.999807	44.605	.049
29			1.000438	44.633	
30			1.000368	44.630	
31	.999906	44.610	1.000353	44.630	-.020
33	.999350	44.585	1.000307	44.628	-.043
34	.999520	44.592	1.000050	44.616	-.024
35			1.000480	44.635	
39	.999563	44.594	1.000210	44.623	-.029
45	.999514	44.592	1.000050	44.616	-.024
46			.999415	44.588	
48			.999168	44.577	
49			.999800	44.605	
50	.999881	44.609	.999304	44.583	.026
51			.999060	44.572	
52	.999452	44.589	.999321	44.584	.005
Average		44.6065		44.6099	-.0048
Std. dev.		.021		.022	.030*

* Since the numbers in this column are differences of two measurements, the standard deviation found for this column is $\sqrt{2}$ times that for single measurements. Consequently, the standard deviation for single measurements derived from the differences is $(.030)/\sqrt{2} = .021$. This value does not include possible variability between samples.

The last column of Table 4 is used for two purposes: a) to obtain an additional estimate of the standard deviation among replicates, and b) to test whether a significant systematic shift has occurred between the two sets ("first analysis" and "second analysis"). The estimate of the standard deviation, converted to a single measurement basis is .021 and is consistent with that obtained previously (s = .018). As to a possible shift, there is no evidence for such an occurrence. (A test of significance can be carried out as follows:

$$t = \frac{-.0048}{.030/\sqrt{10}} = -.50$$

This value is not significant, when compared with the critical value of Student's t, for 10-1 = 9 degrees of freedom.)

The standard deviations, .021 and .022, for the two sets of values in Table 4 are mutually consistent. Moreover, since they are of the same order of magnitude as the measurement error (as derived from replicate measurements on the same sample), it may be concluded that no measurable heterogeneity exists between the cylinders of this lot.

The best average value for the concentration of the lot is:

$$\frac{(44.6065 \times 10) + (44.6099 \times 21)}{10 + 21} = 44.6088$$

The standard error of this overall average is:

$$\frac{.022}{\sqrt{31}} = .0040$$

This standard error does not include calibration error, errors in the value of the SRM and in the value of internal reference standard.

4. Auditor's Calibration Data

Table 5 shows the auditor's calibration results.

TABLE 5

SRM No.	Concentration*	Signal (counts)
1677	9.79 ± .09	19,688
1678	45.3 ± .5	91,642
1679	97.1 ± .8	197,990
1680	476. ± .4	979,130

* The ± values are the total uncertainties given in the SRM certificates.

The sensitivities (signal/concentration) are successively:

2011, 2023, 2039 and 2057 counts/ppm.

These values indicate a trend due, either to the presence of a blank or to curvature, or to both.

A regression analysis shows a slight amount of curvature, but otherwise the calibration data appear satisfactory. Since the samples are of the order of magnitude of SRM 1678, the latter will be used for conversion of signal to concentration, through the equation:

signal = 2023 (concentration).

5. Auditor's Sample Measurements

The auditor made 10 replicate analysis on each of two cylinders, no. 48 and no. 29. The results are shown in Table 6.

TABLE 6

Cylinder 48		Cylinder 29	
Signal	Concentration	Signal	Concentration
89866	44.422	89781	44.380
90044	44.510	90121	44.548
89495	44.239	89874	44.426
89570	44.276	90050	44.270
90024	44.500	89558	44.270
89997	44.487	89874	44.426
89568	44.275	90226	44.600
89708	44.344	89888	44.433
89742	44.361	89987	44.482
89852	44.415	89655	44.318
Average	44.3729		44.4396
Std. dev.	0.099		0.101

6. Evaluation of Uncertainties and Intercomparison of Results

a. Internal Comparison of Auditor's Results

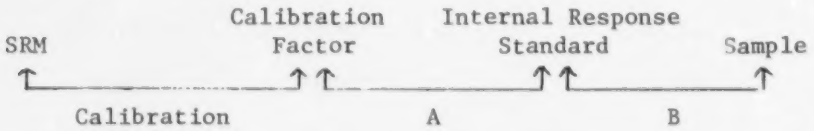
The standard deviation of a single measurement made by the auditor is 0.10. The results for cylinders 48 and 29 may be compared by Student's *t*-test:

$$t = \frac{44.3829 - 44.4396}{.100\sqrt{\frac{1}{10} + \frac{1}{10}}} = -1.27$$

The *t*-value is not significant. There is therefore no evidence of heterogeneity between the two cylinders.

b. Total Uncertainty of Producer's Values

The value of each sample obtained by the producer is obtained by a procedure represented by the following diagram:



The total error in the sample value is composed of four parts:

1) the uncertainty in the SRM value
2) the uncertainty in the calibration experiment
3) the uncertainty due to comparison A
4) the uncertainty due to comparison B

We use the rule (derived from the law of propagation of errors) that the square of the relative error of the final value is equal to the sum of the squares of the relative errors of the components.

More specifically, if $\hat{c}_i$ is the final concentration value obtained for a particular sample (denoted by the subscript *i*) in the lot, we have (from step B):

$$\hat{c}_i = R_i \; C_{Ref} \qquad (1)$$

Where R_i is the ratio of signals for sample *i* to the reference sample, and C_{Ref} is the concentration attached to the reference sample. But C_{Ref} is obtained in step A by averaging ten values obtained each as

$$\frac{\text{Signal}}{k} \qquad (2)$$

where k is the calibration value derived from the calibration experiment. In our case, k = 1.205. The average of the ten measurements may be described by

$$C_{Ref} = \frac{\bar{S}}{k} \tag{3}$$

where $\bar{S}$ is the average of ten replicate signal values. Combining (1) and (3) gives

$$\hat{c}_i = R_i \frac{\bar{S}}{k} \tag{4}$$

The value of k is obtained experimentally from a single signal value divided by the concentration of the SRM. Thus we may write:

$$k = \frac{S_o}{C_o} \tag{5}$$

where C_o is the concentration attached to the SRM by the certificate and S_o is the signal corresponding to it.

Combining (4) and (5), we obtain finally:

$$\hat{c}_i = R_i \bar{S} \frac{C_o}{C_o} \tag{6}$$

The law of propagation of errors gives:

$$\left(\frac{\sigma_{\hat{c}_i}}{\hat{c}_i}\right)^2 = \left(\frac{\sigma_{R_i}}{R_i}\right)^2 + \left(\frac{\sigma_{\bar{S}}}{\bar{S}}\right)^2 + \left(\frac{\sigma_{S_o}}{S_o}\right)^2 + \left(\frac{\sigma_{C_o}}{C_o}\right)^2 \tag{7}$$

The first term of the right side represents step B; the second term step A and the third term the uncertainty of the calibration experiment itself. The last term represents the uncertainty of the SRM used for calibration.

We now estimate these four components.

1) $\frac{\sigma_{R_i}}{R_i}$ (step B) is obtained from the last column of Table 4:

$$\frac{\sigma_{R_i}}{R_i} = \frac{.021}{44.61} = 4.71 \times 10^{-4} \tag{8}$$

2) $\frac{\sigma_{\bar{S}}}{\bar{S}}$ (step A) is obtained from the calculations derived from Table 3:

$$\frac{\sigma_{\bar{S}}}{\bar{S}} = \frac{.0057}{44.62} = 1.28 \times 10^{-4} \qquad (9)$$

3) $\frac{\sigma_{S_o}}{S_o}$ (calibration experiment) has not been measured, but we can assume the same precision as in step A for a single measurement:

$$\frac{\sigma_{S_o}}{S_o} = \frac{.018}{44.62} = 4.03 \times 10^{-4} \qquad (10)$$

4) $\frac{\sigma_{C_o}}{C_o}$ (uncertainty of SRM) is derived from the uncertainty given in the certificate. We will assume that this stated uncertainty is equal to two standard deviations. Thus:

$$\frac{\sigma_{C_o}}{C_o} = \frac{1}{2}\ \frac{0.5}{44.9} = 55.68 \times 10^{-4} \qquad (11)$$

Adding the squares we have:

$$\left(\frac{\sigma_{\hat{c}_i}}{\hat{c}_i}\right)^2 = \left[(4.71)^2 + (1.28)^2 + (4.03)^2 + (55.68)^2\right] \times 10^{-8}$$
$$= 3140 \times 10^{-8}$$

Hence:

$$\sigma_{\hat{c}_i}/\hat{c}_i = 56 \times 10^{-4}$$

Since all $\hat{c}_i$ are approximately the same and equal to $\hat{c}_i = 44.62$, we obtain

$$\sigma_{\hat{c}_i} = 56 \times 10^{-4} \times 44.62 = 0.25 \qquad (12)$$

We see that the predominant component of uncertainty, in this case, is that of the SRM.

c. Comparison of Producer's and Auditor's Values

By a calculation similar to that above, we obtain, for the auditor's value for a particular cylinder, say c_i^*:

$$\left(\frac{\sigma_{c_i^*}}{c_i^*}\right)^2 = \left(\frac{\sigma_{\overline{ct}}}{\overline{ct}}\right)^2 + \left(\frac{\sigma_{ct}}{ct}\right)^2 + \left(\frac{\sigma_{C_o^*}}{C_o^*}\right)^2 \qquad (13)$$

Step A is not present for the auditor's data. The symbol ct represents a count and $\overline{ct}$ an average of ten counts; C_o^* represents the value given by the certificate for the SRM used in the calculation of the calibration factor. We have:

$$\left(\frac{\sigma_{c_i^*}}{c_i^*}\right)^2 = \left(\frac{.10/\sqrt{10}}{44.4}\right)^2 + \left(\frac{.10}{44.4}\right)^2 + \left(\frac{.25}{45.3}\right)^2$$

$$= (7.12\times10^{-4})^2 + (22.52\times10^{-4})^2 + (55.19\times10^{-4})^2$$

$$= 3604\times10^{-8} = (60\times10^{-4})^2$$

Since $c_i^* = 44.4$ for both samples analyzed by the auditor, we have:

$$\sigma_{c_i^*} = 60\times10^{-4}\times44.4 = .27$$

We now obtain the following results (Table 7):

TABLE 7*

	Sample 48	Sample 29
Producer	44.58 ± .25	44.63 ± .25
Auditor	44.38 ± .27	44.44 ± .27

* The ± values represent standard errors in this table.

It is apparent that the result obtained by the auditor for each sample is not significantly different from that of the producer for the same sample. Thus, the auditor's value in this case, substantiate those provided by the producer.

In general it may be assumed that there is no significant difference between the concentration claimed by the producer and that found by the auditor if the following expression is satisfied.

$$c_i - c_i^* \leq 2\sqrt{\sigma_{c_i}^2 + \sigma_{c_i^*}^2}$$

APPENDIX B

REPORT FORMS

The following forms, A and B, are suggested report forms which will be made available to both the producer and the auditor.

FORM A. Report of Analysis of Certified Reference Materials

(Producer)

Prepared by: (Company name & address)

(Individual preparing report & date)

Description:

Composition:

Corresponding SRM No.:

Date Blended:

Date Transferred:

Analysis

SRM's Used as Calibrants:

No.	Sample No.	Cylinder No.	Concentration	Purchase Date
1.				
2.				
3.				
4.				
5.				

FORM A (Continued)

Brief Description of Methods:

Brief Description of Calibration Procedure:

Calibration Data:

	SRM No.	Signal or Sensitivity (Identify)
1.		
2.		
3.		
4.		
5.		

Results

Analysis of Internal Standard (if used)

Sample No. Cylinder No.

	Concentration	Date of Analysis
1.		
2.		
3.		
4.		
5.		
6.		
7.		
8.		
9.		
10.		

Average _____ s.d. _____

FORM A (Continued)

Analysis of CRM's

Concentration on Date Shown

Sample No. Cylinder No.

Average _____ s.d._____

FORM B. Report of Analysis of Certified Reference Materials

(Auditor)

Prepared by:

Description:

Analysis:

SRM's Used as Calibrants:

No.	Sample No.	Cylinder No.	Concentration	Purchase Date
1.				
2.				
3.				
4.				
5.				

Brief Description of Method:

Brief Description of Calibration Procedure:

Calibration Data:

SRM No.	Signal or Sensitivity (Identify)
1.	
2.	
3.	
4.	
5.	

FORM B (Continued)

Analysis of CRM

Sample No.		Sample No.	
Cylinder No.	Concentration	Cylinder No.	Concentration
Ave. _____		Ave. _____	
s.d. _____		s.d. _____	

APPENDIX C

CARBON MONOXIDE

A. SRM's

The available SRM's are as follows:

CO in N_2

SRM No.	Nominal Concentration
1677	10 ppm
2635	25 ppm
1678	50 ppm
1679	100 ppm
2636	250 ppm
1680	500 ppm
1681	1000 ppm
2637	2500 ppm
2638	5000 ppm
2639	1 %
2640	2 %
2641	4 %
2642	8 %

CO in Air

SRM No.	Nominal Concentration
2612	10 ppm
2613	18 ppm
2616	42 ppm

The concentrations shown are in parts per million (ppm) by mole and in mole percent. The actual concentration of a particular SRM may differ by more than several percent relative from the nominal value and it is therefore essential that the exact concentration of the SRM to be duplicated be known before attempting the preparation of the CRM.

The maximum permissible levels of impurities in the CRM are as follows:

Water Vapor	10 ppm
Methane	1 ppm (CO in N_2)
Methane	5 ppm (CO in air)
Carbon Dioxide	5 ppm (CO in N_2)
Carbon Dioxide	400 ppm (CO in air)

B. Cylinders

CRM's must be packaged in new aluminum cylinders or in used aluminum cylinders which have been used exclusively for mixtures containing carbon monoxide in nitrogen or air. The history of any cylinder to be reused must be known and confirmation must be obtained by analysis that the contents have not been diluted or contaminated. Cylinders to be reused must contain sufficient gas from the last filling to allow an analysis. The concentration must lie within ± 1 percent relative of the original analysis. The cylinder must be evacuated before refilling and the concentration of the CRM to be added must lie within 2 orders of magnitude (± 100% relative) of the concentration of the CRM previously contained.

C. Preparation of Analysis

Prepare a lot of at least 10 cylinders all at identical concentration. The concentration of carbon monoxide must lie within ± 1 percent relative of the concentration of the specific SRM with which the lot is to be compared. Analyze a representative number of cylinders by direct comparison to the SRM or by comparing cylinders in the lot to a single sample selected at random from the lot (internal standard from the lot). Analyze each sample at least two times. Calculate the average of all results for all samples and calculate the standard deviation of the average.

The lot should be put aside to "incubate" for at least one month after which time all samples in the lot are analyzed. The results for the first and second analyses should be statistically identical. If the two analyses are the same, then it may be assumed that the lot is homogenous and stable. If the analysis was performed by direct comparison to the SRM, then the analytical value for the sample will be the certified value. If the analyses were performed by comparison to an internal standard for the lot, then it will be necessary to determine the concentration of the internal standard. This is done by repeated comparison of the internal standard to the SRM. The concentration measured ratio of each sample to the internal standard to obtain the concentration of each sample.

The uncertainty of the CRM is composed of the uncertainty of the SRM, and any random errors introduced by the analysis of the CRM. The error of the SRM, E, is given on the certificate for the particular cylinder and is defined as the estimated upper limit of the total uncertainty. The estimated upper limit of the uncertainty for the CRM should be calculated as follows:

$$E_2, \text{ (Total Error)} = 2\sqrt{\left(\frac{E_{SRM}}{2}\right)^2 + a^2 + b^2 + c^2}$$

where E_2 is the uncertainty of the CRM; a is the imprecision of intercomparison of the internal standard with the lot; b is the imprecision of intercomparison of the internal standard and the SRM; and c is the error of the calibration experiment if applicable (see Appendix A).

The following table lists the methods of analysis which are applicable to the analysis of CRM's of carbon monoxide in nitrogen or air. The method chosen is not necessarily limited to those shown providing that the method chosen is of adequate sensitivity, precision and linearity. The precision and sensitivity are evaluated during the analysis described earlier and are reflected directly in the "imprecision of intercomparison". The linearity must be defined in the concentration range between the CRM and the SRM.

TABLE 1. METHODS FOR THE INTERCOMPARISON OF CRM'S AND SRM'S OF CARBON MONOXIDE IN AIR OR NITROGEN

Method	Concentration of CO
Gas Chromatography - TC Detector	8% - 0.5%
Gas Chromatography - Ultrasonic Detector	1% - 0.05%
Gas Chromatography followed by catalytic reduction to methane with flame ionization detector	1% - 10 ppm
Non-dispersive Infrared	8% - 10 ppm

D. Period of Certification

Experience at NBS indicates that carbon monoxide mixture contained in aluminum cylinders are stable for periods of three years or more. If no change in concentration of the CRM's is indicated by the results of the producer's first and second analysis, then stability for a period of two years from the date of the second analysis is assured with a high degree of probability. Any samples not sold within one year of the second analysis should be reanalyzed and the period of certification should be appropriately extended.

E. Recertification

CRM's of carbon monoxide in nitrogen or air which have exceeded the period of certification may be recertified by the original supplier according to the following provisions.

1. The pressure remaining in the cylinder must be greater than 500 psi (3.4 kPa).

2. The ratio of the signal generated by the CRM when compared to the original internal standard must be the same as when originally measured within the limits of uncertainty generated by both sets of measurements.

3. The concentration of the internal standard, determined by comparison to the SRM with which it was originally compared, must be the same within the limits of precision of the comparison.

4. The concentration of the SRM must be known either by comparison with a new SRM or the original SRM must have been recently recertified by NBS.

5. If either the original SRM or the internal standard no longer exists then no recertification can be made.

6. The uncertainty to be assigned to the recertified value must include the added uncertainty, if any, of the recertification process.